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| (21) International Application Number: PCT/US96/18841 (22) International Filing Date: 12 November 1996 (12.11.96) (71) Applicant (for all designated States except US): MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BENNETT, Gregory, Scott [US/DE]; Fernholz 8A, D-40883 Ratingen (DE). THYSEN, Andre, Peter [DE/DE]; Moorenring 17, D-47906 Kempen (DE). RIEDER-OTTERBURG, Suzanne, Helene [DE/DE]; Allensteinstrasse 27, D-41564 Kaarst (DE). HAAK, Christopher, A. [US/US]; 7504 46th Street North, Oakdale, MN 55128 (US). KARIM, Naimul [BD/US]; 2360 Linwood Court, Maplewood, MN 55119 (US). (74) Agents: SKOLNICK, Steven, E. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). | | (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> |
| (54) Title: THERMOSETTABLE PRESSURE SENSITIVE ADHESIVE (57) Abstract <p>The invention refers to a photopolymerizable precursor of a pressure-sensitive thermosettable adhesive, said precursor comprising: (i) from about 30 % to about 80 % by weight with respect to the mass of the precursor of a photopolymerizable component, comprising a monomeric or prepolymeric syrup, said component exhibiting an overall solubility parameter of between 10 and 11 and comprising (A) at least 30 % by weight with respect to the mass of the photopolymerizable component (i) of one or more ethylenically unsaturated monomers with a solubility parameter of between 10 and 11.5 and less than 10 % by weight with respect to the mass of component (i) of one or more ethylenically unsaturated compounds with a solubility parameter of more than 11.5, or (B) at least 50 % by weight with respect to the mass of the photopolymerizable compound (i) of one or more ethylenically unsaturated monomers with a solubility parameter of between 9.5 and 11.5 and 10-30 % by weight with respect to the mass of the photopolymerizable component (i) of one or more ethylenically unsaturated compounds with a solubility parameter of between 11.5 and 12.5 provided that in case (B) the precursor comprises between 3-15 % by weight with respect to the mass of the precursor of one or more polymers with a solubility parameter of 10-12.5; (ii) from about 20 to about 70 % by weight with respect to the mass of the precursor of one or more epoxy resins and/or monomers; (iii) an effective amount of a photoinitiator; and (iv) an effective amount of one or more nucleophilic latent hardeners for the epoxy resins and/or epoxy-containing monomers which are selected to provide an onset temperature of the epoxy curing reaction of between 40-100 °C when subjecting the adhesive to a DSC scan at a rate of 20 °C/min. The invention furthermore refers to thermosettable adhesives which are obtainable by photopolymerization of said precursor and to thermoset adhesives which are obtainable by thermal curing of said thermosettable adhesives. The thermosettable adhesive of the invention is particularly useful for bonding a plastic substrate to other substrates such as metal, glass, ceramic, wood and plastics.</p> | | |

THERMOSETTABLE PRESSURE SENSITIVE ADHESIVE**BACKGROUND OF THE INVENTION****5 Field of the invention**

The present invention refers to a thermally-curable epoxy/acrylate based pressure-sensitive adhesive which has an onset temperature of the epoxy curing reaction of below 100°C and to the photopolymerizable precursor of such adhesive. The present invention furthermore refers to a method for bonding a plastic surface to another surface by using such adhesive and to the assemblies thus obtained. The invention furthermore refers to an assembly comprising two plastic surfaces exhibiting a high overlap shear strength.

Background of the invention

15 Thermosettable epoxy-acrylate based pressure-sensitive adhesives, the acrylate component of which comprises from about 30% to about 80% by weight of a photopolymerizable monomeric or prepolymeric syrup containing an acrylic acid ester of a non-tertiary alcohol, and a moderately polar copolymerizable monomer, have been described in US 5,086,088. The hardener for the epoxide component
20 preferably is an amine hardener, and a curing temperature of, for example, 140°C is applied for 20 or 40 minutes (see Example 41 of US '088). The pressure-sensitive adhesive tapes are proposed for use in the automotive industry. In a specific embodiment which is termed as roof ditch molding, the pressure-sensitive adhesive tape is first applied to the roof molding and fastened to the body of a car. The
25 pressure-sensitive adhesive tape is thermoset in a subsequent curing cycle.

US 4,552,604 relates to a method for bonding together two surfaces selected from the group consisting of metals, ceramics or wood using a thermosettable epoxy/acrylate based pressure-sensitive adhesive which optionally is tacky. The
30 specification discloses a broad range of acrylate components and uses in the examples moderately polar components such as 1-phenoxy-2-hydroxypropyl

of US '088 and US '604 are high in polarity which makes them less favourable for bonding of non-polar substrates such as plastics. The acrylate-containing monomeric or prepolymeric syrup described in WO '328, sometimes exhibits a limited solubility for the thermosettable resin, and the mechanical properties of the thermoset adhesive do not always meet all practical requirements to a sufficient and/or desirable degree.

There was therefore a need for providing a thermosettable pressure-sensitive adhesive having an onset temperature of the epoxy curing reaction of not more than 100°C so as to render the adhesive curable at reduced temperatures and/or for reduced times and to facilitate bonding of thermally-sensitive substrates such as plastics.

There was furthermore a need for providing a thermosettable pressure-sensitive adhesive which has good cured-state adhesive properties to low energy surfaces such as plastics and allows for the preparation of assemblies comprising at least one low-surface energy substrate bonded to another substrate with the thermoset adhesive, which exhibits advantageous mechanical properties and, in particular, a high overlap shear strength.

Short description of the invention

The invention relates to the photopolymerizable precursor of a thermosettable pressure-sensitive adhesive said precursor comprising:

- (i) from about 30% to about 80% by weight with respect to the mass of the precursor of a photopolymerizable component comprising a monomeric or a prepolymeric syrup said component exhibiting an overall solubility parameter of between 10 and 11 and comprising
 - (A) at least 30% by weight with respect to the mass of component (i) of one or more ethylenically unsaturated monomers with a solubility parameter of

The invention furthermore refers to an assembly comprising two plastic surfaces which are bonded with a thermally-cured pressure-sensitive adhesive, the precursor of which comprises a blend of an acrylate-based pressure-sensitive adhesive and one or more thermosettable epoxy resins and/or monomers and is cured at a temperature above the onset temperature of the epoxy curing reaction to give an overlap shear strength of the assembly of at least 3 MPa.

Detailed description of the invention

The present invention refers to a thermosettable pressure-sensitive adhesive which is obtainable by photopolymerization of the corresponding photopolymerizable precursor. The pressure-sensitive adhesive is thermosettable, i.e. can be cured by application of heat to give a thermoset adhesive.

The epoxy/acrylate based thermosettable pressure-sensitive adhesive according to the invention exhibits good adhesion to low energy surfaces and allows for the preparation of assemblies comprising two low energy surfaces or a low energy surface and another surface. Low energy surfaces are defined as polymeric surfaces such as polymethylmethacrylate, polycarbonate, polystyrene and acrylonitrile-butadiene styrene and the like but do not include very low energy surfaces such as polytetrafluoroethylene and polyolefins such as polyethylene. Such assemblies exhibit advantageous mechanical properties and, in particular, a high overlap shear strength. The advantageous mechanical properties are achieved by adjusting the polarity of the photopolymerizable component (i) of the precursor of the thermosettable pressure-sensitive adhesive so that

- the polarity and the dissolution power are low enough, on the one hand, to provide good adhesion of both the uncured and thermally-cured adhesive to low energy surfaces, and
- the polarity and the dissolution power are high enough, on the other hand, to dissolve a sufficiently high amount of the epoxy part (ii) of the thermosettable adhesive so as to provide advantageous mechanical properties of the thermally cured adhesive.

- 10-30% by weight with respect to the mass of the photopolymerizable component (i) of one or more ethylenically unsaturated monomers with a solubility parameter of between 11.5 and 12.5, and
- 3-15% by weight with respect to the mass of the precursor of one or more polymers having a solubility parameter of between 10 and 12.5.

The solubility parameters referred to above and below are calculated according to the technique described in Fedors, Polym. Eng. and Sci., 14 (1974), 147. A list of several common ethylenically unsaturated monomers and their respective Fedors' solubility parameters is shown in Table 1 below. The term 'overall solubility parameter' of the photopolymerizable component (i) used above and below, is defined as the sum of the solubility parameters of the different monomers and repeat units of any photopolymerizable prepolymeric, oligomeric or polymeric constituents of component (i) as weighted by the respective percentage by weight of the monomers and repeat units with respect to the sum of the masses of the monomers and the photopolymerizable prepolymeric, oligomeric or polymeric constituents of component (i).

It was surprisingly found that the photopolymerizable component (i) of the precursor of the thermosettable pressure-sensitive adhesive has to exhibit both in embodiment (A) and (B) a medium overall solubility parameter of between 10-11 and preferably of between 10.0 and 10.8 and more preferably of between 10.1 and 10.6.

In embodiment (A) the precursor must additionally comprise at least 30% of one or more ethylenically unsaturated compounds with a medium solubility parameter of between 10-11.5, preferably of between 10.2 and 11.3 and more preferably of between 10.3 and 11.2.

Contrary to this, precursors of thermosettable pressure-sensitive adhesives where the photopolymerizable component (i) meets the requirement of a medium overall

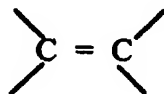
more ethylenically unsaturated monomers with a moderately high solubility parameter of between 11.5 and 12.5 and at least 50% by weight with respect to the mass of component (i) of one or more ethylenically unsaturated monomers with a moderately low or medium solubility parameter of between 9.5 and 11.5.

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The photopolymerizable component (i) of the precursor of embodiment (B) often exhibits an advantageous solubility behaviour with respect to the epoxy component (ii) which is due to the presence of a substantial amount of one or more ethylenically unsaturated monomers with a moderately high solubility parameter of between 11.5 and 12.5 in component (i). It was surprisingly found that the solubility of the hardener component (iv) in the precursor can be sufficiently suppressed in spite of the presence of the ethylenically unsaturated monomers with a moderately high solubility parameter in component (i) by adding 3-15% by weight with respect to the mass of the precursor of one or more polymers with a solubility parameter of between 10 to 12.5. The average molecular weight M_w of the polymers is preferably between 50,000 to 500,000 g/mol.

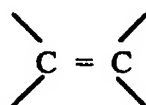
Below the limit of 3% by weight of the polymer additive the solubility of the hardener component in the precursor is too high which results in disadvantageous shelf-life and stability in case the latency of one or more of the hardener compounds is based on solvent effects, crystallinity and/or encapsulation. Above the limit of 15% by weight of the polymer additive, the viscosity of the precursor typically is too high which results in disadvantageous handling properties.

Above and below the term ethylenically unsaturated monomers refers to compounds comprising one or more groups



Although the properties of the precursor of the thermosettable pressure-sensitive adhesives and of the photopolymerized adhesive according to embodiment (A) are sensitive to the addition of polar copolymerizable monomers with a Fedors solubility of more than 11.5, especially of more than 12.5 and, in particular, of more than 13, a small amount of less than 10%, and more preferably of not more than 7.5% by weight with respect to the mass of the photopolymerizable component (i) of the precursor may occasionally be added to improve the solubility of the epoxy component (ii) of the precursor in the photopolymerizable component (i). Copolymerizable monomers with a Fedors solubility of more than 13 should not be added in an amount of more than 5% and more preferably not more than 3% by weight with respect to the mass of component (i) of the precursor. Preferred examples of a suitable strongly polar acrylate monomer are butoxy acrylate and N-vinylcaprolactam.

Although component (i) of embodiment (A) is preferably acrylate-based, i. e. preferably contains at least 50% by weight with respect to the mass of component (i) of one or more acrylic esters of non-tertiary alcohols, it may also comprise other ethylenically unsaturated copolymerizable monomers, oligomers and/or polymers comprising one or more groups



Examples of preferred non-acrylate copolymerizable monomers having a solubility parameter of between 10 and 11.5 are N-octyl acrylamide and vinyl acetate and, in particular, N-octyl acrylamide.

Examples of suitable non-acrylate copolymerizable monomers with a solubility parameter of more than 11.5 are N-vinyl caprolactam, N,N-dimethylacrylamide and butoxy acrylate.

partially prepolymerized, initiation is preferably conducted with a part of the photoinitiator component (iii). The premix of (i) and part of (iii) is then partially prepolymerized to a syrup exhibiting a room temperature viscosity in the range from about 100 to about 20,000 cps and, more preferably, from about 300 to 5,000 cps.

- 5 The weight percentages given above and below for ethylenically unsaturated monomers comprise both unreacted and partially prepolymerized ethylenically unsaturated monomers.

Photopolymerizable component (i) of embodiment (B)

- 10 The ethylenically unsaturated monomers with a solubility parameter of between 9.5 and 11.5 of the photopolymerizable component (i) of embodiment (B) preferably are acrylates. These are preferably selected from a group consisting of monofunctional acrylic or methacrylic esters of a non-tertiary alcohol such as iso-butyl acrylate, butyl acrylate, propyl acrylate, ethyl acrylate, iso-bornyl acrylate,
15 tetrahydro-furfuryl acrylate, methyl acrylate and 2-phenoxy-ethyl acrylate. The ethylenically unsaturated monomers have a solubility parameter of between 9.5 and 11, more preferably of between 9.5 and 10.5 and especially preferably of 9.5 and 10. Especially preferred is a smaller group of monofunctional acrylic esters comprising butyl acrylate, propyl acrylate and iso-bornyl acrylate.

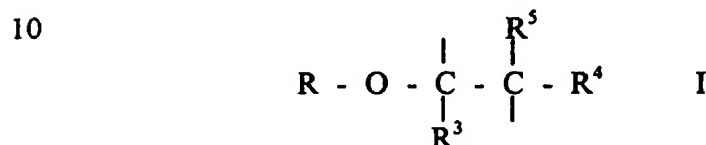
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- The photopolymerizable component (i) of the precursor of the thermosettable pressure-sensitive adhesive according to embodiment (B) additionally comprises from 10 to 30% and preferably from 10 to 20% by weight with respect to the mass of component (i) of one or more copolymerizable ethylenically unsaturated
25 monomers having a solubility parameter of between 11.5 and 12.5 and preferably of between 12 - 12.5 to improve the solubility of the epoxy component (ii) of the precursor in the photopolymerizable component (i). Examples of preferred copolymerizable monomers with a solubility parameter of between 11.5 and 12.5 are N-vinyl caprolactam and N,N-dimethylacrylamide.

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for example, between 50,000 - 500,000 g/mol and should be essentially uncrosslinked in order to enhance the solubility of the polymer in the precursor or the photopolymerizable component (i), respectively. The polymer additives should furthermore be preferably essentially "dead", i.e. free or basically free from unsaturated or chain transferring groups in order to avoid crosslinking or chain transfer reactions with component (i) of the precursor.

Examples of preferred polymers are those that comprise units of formula I



Above and below polymers comprising units of formula I are also termed as polymers of formula I.

R is preferably R¹-CO- with R¹ being preferably methyl, ethyl, propyl, butyl, pentyl, methoxy, ethoxy, propoxy or partially or fully halogenated methyl. R especially preferably denotes CH₃-CO-. Polymers comprising units of formula I wherein R is R¹-CO- are termed below and above as vinyl ester type polymers.

R can also be R² with R² being preferably methyl, ethyl, propyl, butyl or pentyl. Polymers comprising units of formula I wherein R is R² are termed below and above as vinyl ether type polymers.

R³, R⁴ and R⁵ are preferably independently from each other hydrogen, methyl or ethyl. One of R³, R⁴ and R⁵ may also preferably be methoxy, ethoxy, propoxy, partly or fully halogenated methyl or a fluoro or chloro group.

The polymer comprising units of formula I may be a homopolymer or a copolymer of two or more comonomers. The polymer used in the precursors according to the

The polymer or polymers are preferably selected so that they are compatible with the photopolymerizable component (i) and so that a polymer being obtainable by polymerization of component (i) including the polymer or polymers, has a glass transition temperature of between -20 and 40 °C. In an especially preferred embodiment the compounds of component (i) are selected so that the polymer obtained by photopolymerization of component (i) including the polymer or polymers, has a glass transition temperature of between 230 and 345 K, more preferably of between 240 and 335 K and especially preferably of between 240 and 320 K. The glass transition temperature of the photopolymer component (i) including the polymer(s) can be estimated by using the Fox equation mentioned above.

It is to be understood that other polymers can be used and that the polymer of formula I and the specific polymers listed above illustrate the invention without limiting it.

Component (i) of embodiment (B) can also comprise copolymerizable oligomers or polymers such as, for example, macromonomers.

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The photopolymerizable component (i) of embodiment (B) can be unpolymerized or partly prepolymerized as described above for embodiment (A). The photopolymerizable component of embodiment (B) is, however, preferably unpolymerized. Its viscosity can be modified if desired by dissolving part or all of the polymer additive with a solubility parameter of between 10 and 12.5. The weight percentages given above and below for ethylenically unsaturated monomers comprise both unreacted and partially prepolymerized ethylenically unsaturated monomers, if any.

the reaction product of epichlorohydrin and p-amino phenol, the reaction product of epichlorohydrin and glyoxal tetraphenol and the like. Cycloaliphatic epoxies are less preferred.

- 5 Suitable commercially available diglycidic ethers of bisphenol-A are Ciba Geigy Araldite TM 6010, Dow Chemical DER TM 331, and Shell Chemical Epon TM 825, 828, 826, 830, 834, 836, 1001, 1004, 1007, etc.

- 10 A polyepoxidized phenol formaldehyde novolac prepolymer is available from Dow Chemical as DEN TM 431 and 438 and from Ciba Geigy as CY-281 TM, and a polyepoxidized cresol formaldehyde novolac prepolymer is available from Ciba Geigy as ECN TM 1285, 1280 and 1299.

- 15 A polyglycidyl ether of polyhydric alcohol is available from Ciba Geigy, based on butane-1,4-diol, as Araldite TM RD-2; and from Shell Chemical Corporation based on glycerine, as Epon TM 812.

- 20 Suitable commercially available flexible epoxy resins include polyglycol diepoxies, DER TM 732 and 736, from Dow Chemical Company, diglycidyl ester of linoleic dimer acid, Epon TM 871 and 872 from Shell Chemical Company, and diglycidyl ester of a bisphenol in which the aromatic rings are linked by a long aliphatic chain, Lekutherm TM X-80, from Mobay Chemical Company.

- 25 High functional epoxy resins (i.e. functionality greater than 2) which can be used include, for example, a solid epoxy novolac resin, DEN TM 485 from Dow Chemical Company, a tetrafunctional solid epoxy resin, Epon TM 1031 from Shell Chemical Company, and N,N,N',N'-tetraglycidyl-4,4'-methylenebisbenzenamine, Araldite TM MY 720 from Ciba Corporation. Difunctional epoxy resins which can be used include, for example, a solid resin, N,N,N',N',-tetraglycidyl-a,A'-bis(4-aminophenyl)-p-diisopropylbenzene, HPT TM 1071 from Shell Company, solid
30 diglycidyl ether of bisphenol-9fluorene, HPT TM 1079 from Shell Chemical

Latent nucleophilic hardener component (iv)

The precursor of the thermosettable pressure-sensitive adhesives according to the present invention comprises one or more latent nucleophilic hardeners for the epoxy component (ii) which react with the oxirane ring of the epoxy compounds of component (ii) in an effective amount to cause cross-linking of the epoxy component (ii). It is an essential feature of the present invention that the hardener compounds are latent and that they are selected to provide when subjecting the photopolymerized thermosettable pressure-sensitive adhesive to a DSC scan at a rate of 20°C/min, an onset temperature of the epoxy curing reaction of below 100°C.

The term "latent" means that the hardener compound is essentially unreactive at room temperature, but reacts rapidly to effect curing once the onset temperature of the epoxy curing reaction has been exceeded. The onset temperature, which is measured by the method cited under test methods, is above room temperature and below 100°C, preferably between 40 - 90°C and more preferably between 40 - 80°C. Rapid reaction means that the epoxy curing reaction is completed to a degree of at least 80% of full curing within 2 hours, preferably within 1 hour and more preferably within 30 minutes or less when subjecting the photopolymerized, thermosettable adhesive to a temperature of about 10°C above the onset temperature.

The preferred lower limit of 40°C is chosen to allow for convenient handling of the thermosettable pressure-sensitive adhesive at room temperature, whereas the upper limit of 100°C ensures that the thermosettable pressure-sensitive adhesive of the present invention can be used for bonding plastic substrates. The lower limit of the onset temperature range can also be below 40 °C but has to be chosen to ensure that the hardener is essentially unreactive at room temperature.

The hardener compounds used in the present invention are nucleophilic and heat-activatable and preferably contain one or more nitrogen atoms with at least one

It has also been suggested, for example, in US 5, 310, 840 to use electrophilic, UV-activatable hardener compounds for curing acrylate/epoxy based systems. These hardener compounds are disadvantageous because they have to be added to the thermosettable pressure-sensitive adhesive after the photopolymerization of component (i) has been carried out and, in addition, they must be UV-active before the thermal curing can be carried out.

The degree of latency is reflected in the shelf-life of the thermosettable pressure-sensitive adhesives. The percentage of remaining epoxy curing reaction preferably is at least 80%, more preferably at least 90% after 8 weeks, more preferably at least 80% after 20 weeks and especially preferably at least 80% after 1 year of storage at room temperature. The advantageous shelf-life and storage times are due to the composition of the photopolymerizable component (i) which exhibits a moderate overall solubility parameter of between 10 and 11 and is essentially based on compounds with a moderate solubility parameter of between 10 and 11.5.

The degree of curing of the adhesive can be measured and the percentage of the remaining epoxy cure reaction estimated by standard differential scanning calorimetry techniques such as those described in Thermal Characterization of Polymeric Materials, Edith A. Turi, Ed. (Academic Press, 1981), in particular, in Chapter 5, "Thermosets", pp 435-563.

The latent hardener compounds which are useful in the present invention are preferably selected from a group of compounds according to formula II

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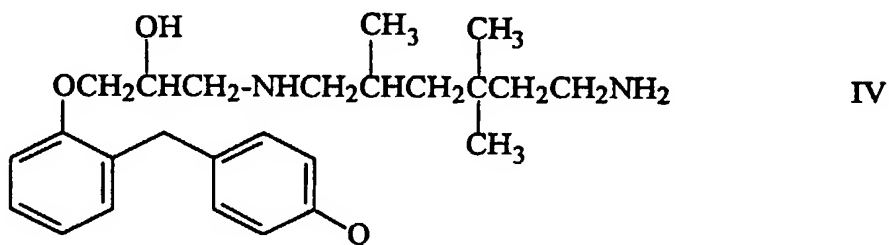
wherein R is a mono- or multivalent organic residue, X_i is, independently from one another, a linear or branched alkyl group with at least 8 C atoms wherein at least one of the $-\text{CH}_2-$ groups is replaced with a $-\text{NH}-$ group and/or which exhibits a

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X_i preferably independently from one another comprises at least 8 and more preferably at least 10 CH_2 groups which may be substituted independently from each other with hydroxyl and halogen, and which may be replaced with $-\text{O}-$, $-\text{CO}-$, $-\text{NH}-$ or $\text{N alkyl}-$ with the proviso that two O or two N atoms are not directly linked.

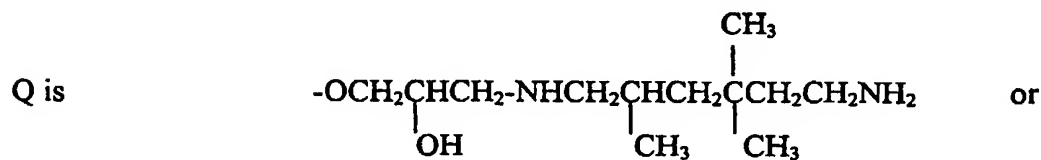
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Especially preferred are the following compounds according to formula IV

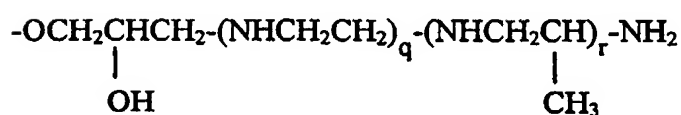


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wherein



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and q and r independently are 1, 2, or 3 and $q + r$ is 1, 2, 3, 4 or 5.

The compounds of formulae II or IV can be obtained by conventional methods. The compounds of formula IV can be obtained, for example, by reacting an aliphatic amine of formula

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temperatures in the temperature range of 40-100°C, the curing time may be up to two hours. At temperatures of 85 °C, for example, curing times of typically 30 to 60 minutes or less may be applied. The curing time is defined as the time for which 80% or more of the curing reaction has been completed.

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The curing times can be considerably decreased by increasing the curing temperature of the epoxy component to higher temperatures, such as, for example, 100 - 250°C. The greater the difference between the curing temperature applied and the onset temperature of the epoxy curing reaction, the more the curing time will be reduced. It was found that curing times of 30 seconds or less can be obtained when using differences between the actual curing temperature and the onset temperature of the epoxy curing reaction of typically about 100°C or more and more preferably of about 125°C or more.

15 The selection of the actual curing temperature depends on the thermal sensitivity of the substrates to be bonded. When using oven curing the curing temperature of polymeric substrates is typically selected to be less than 100°C and, more preferably, not more than 90°C whereas metallic substrates, for example, allow for higher curing temperatures. With other curing techniques, higher curing
20 temperatures may also be applied to polymeric substrates. Copending European patent application no. 96 112 715.6 filed on August 7, 1996, by Minnesota Mining and Manufacturing Company, U.S.A., describes a hand-held device for adhering, for example, anchoring devices such as metal buttons having a thermosettable adhesive layer, to a substrate using curing temperatures of the thermosettable
25 adhesive layer of up to 300°C. It was found by the present inventors that this device can be used to apply, for example, aluminum buttons like those of Fig. 4 of copending EP '715 to plastic substrates such as polycarbonate or polymethacrylate substrates using a hot bar plate temperature of this device of between 180 and 300°C and contact times of 10 seconds or less. These contact times at the
30 respective hot bar plate temperatures are high enough to result in high overlap shear

(meth)acrylates such as, for example, 1,6-hexanediol diacrylate, tri-methylol-propane triacrylate, pentaerythritol tetraacrylate, and 1,2-ethylene glycol diacrylate, urethane di-, tri- and higher functional (meth)acrylates and other organic materials comprising more than one free radically polymerizable double bond.

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Where a foam-like photopolymerized, thermosettable pressure-sensitive adhesive tape is desired, the precursor of the pressure-sensitive adhesive of both embodiments (A) and (B) may comprise polymeric microspheres. Suitable microspheres are commercially available from Kema Nord Plastics under the trade name "Expancel" and from Matsumoto Yushi Seiyaku under the trade name "Micropearl". When expanded the microspheres have a specific density of approximately 0.02 - 0.036 g/cc. It is possible to include the unexpanded microspheres in the pressure-sensitive adhesive composition and subsequently heat them to cause expansion when they are appropriately processed, but it is generally preferred to mix the expanded microspheres into the adhesive. This process makes it easier to ensure that the hollow microspheres in the final adhesive are substantially surrounded by at least a thin layer of adhesive. Polymeric microspheres having an average diameter of 10 to 200 μm may be blended into the polymerizable composition in amount from about 15% to about 75% by volume prior to coating.

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Also useful are glass microspheres having an average diameter of from 5 to 200 μm , preferably from about 20 to 80 μm . Such microspheres may comprise 5% to 65% by volume of the pressure-sensitive adhesive. Both polymeric and glass microspheres are known in the art. Useful polymeric microspheres are, for example, core/shell fillers comprising a low Tg core polymer and a shell polymer which is compatible with the precursor. Core-shell fillers which are useful additives to the precursor of the present invention comprise, for example, a rubber or a silicone polymer core which is bonded to a polymethylmethacrylate shell polymer. A preferred core/shell polymer is commercially available as Modifier 445006 from Wacker Chemie, Munich, Germany. The pressure-sensitive adhesive layer of the

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The photopolymerizable component (i) of both embodiments (A) and (B) may furthermore comprise macromonomers which are copolymerizable with the respective component (i) such as, for example, the vinyl-terminated polymeric macromonomers described in US 3,786,116 or US 3,842,059.

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In case of the precursor of embodiment (A) the amount of "dead" polymer additives and copolymerizable macromonomers preferably varies between 0 - 7.5% and more preferably between 0 - 5% by weight with respect to the mass of the pressure-sensitive adhesive. These additives are useful, for example, for improving adhesion of the thermally uncured and cured adhesive to various of substrates as well as controlling the viscosity of the precursor to aid coating and processing.

In case of the precursor of embodiment (B) the amount of copolymerizable macromonomers preferably varies between 0 - 5% and more preferably between 0 - 4% by weight with respect to the mass of the pressure-sensitive adhesive.

Other materials which can be blended with the precursor of the thermosettable adhesive of both embodiments (A) and (B) include tackifiers, plasticizers, coloring agents, reinforcing agents, fire retardants, thermally conductive agents, post-curing agents such as post-curing curatives and their accelerators, and the like.

Above and below, the mass percentages of components (i) - (iv) and, optionally, of other components and additives of embodiment (A) and (B) add up to 100% by weight for each precursor and thermosettable or thermoset adhesive, respectively.

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Preferred uses of the thermosettable adhesives of embodiments (A) and (B)

The photopolymerized, thermosettable pressure-sensitive adhesive according to the present invention is preferably used in sheet-like or ribbon-like form such as, for example, as adhesive film or adhesive tape. Sheet-like adhesives can be used, for example, as adhesive sheet segments such as those formed by die-cutting.

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- advantageous mechanical properties and exhibits an overlap shear strength of at least 3 MPa, more preferably of at least 4 MPa and, especially preferably, of 5 MPa or more. Assemblies comprising two plastic surfaces which are bonded with a thermoset adhesive the precursor of which comprises a blend of an acrylate-based pressure-sensitive adhesive and one or more thermosettable epoxy resins and/or monomers and is cured at a temperature above the onset temperature of the epoxy curing reaction of below 100°C to give an overlap shear strength of the assembly of at least 3 MPa, are new and they are subject matter of the present invention.
- 10 Curing at relatively low temperatures of not more than 100°C typically requires curing times of between 30 to 120 minutes or less. The curing times can be decreased by increasing the curing temperature and it was found that higher curing temperatures can be used to adhere, for example, metal bars or metal buttons to plastic substrates using, for example, the hand-held device described in copending
- 15 European patent application no. 96 112 715.6.

It was furthermore found that the photopolymerized thermosettable adhesive of the present invention exhibits advantageous adhesion to various surfaces such as metal, glass or ceramics prior to and after thermal curing and can be used for preparing assemblies such as, for example, metal-metal, glass-metal, glass-glass, metal-ceramic and so on. Many of these assemblies can be prepared at higher curing temperatures.

20

The invention is further illustrated by the following non-limiting Examples. Prior to that some test methods used to characterize the thermosettable and thermoset pressure-sensitive adhesive, respectively, according to the invention will be described. In the examples, percentages given are percents by weight and refer to the mass of the photopolymerizable precursor of the thermosettable adhesive. PPh means parts per hundred resin and refers to the mass of component (i).

25

30

The assemblies were subjected to thermal curing in a forced air oven at 85°C for 45 minutes. Prior to testing, the assemblies were conditioned in a constant temperature room (23°C, 55% relative humidity) for at least 12 hours.

5

2. Plastic/adhesive/plastic

Two coupons (75 mm x 15 mm x 10 mm) of the same plastic material were cleaned with isopropyl alcohol and dried. The assembly was obtained as is described above for the Al/adhesive/Al assemblies.

10

The following plastic materials were used:

- polycarbonate (PC), available as Lexan™, clear, from General Electric Plastic
- 15 - polymethylmethacrylate (PMMA), available as Plexiglas™ (clear) from Rohm & Haas, Darmstadt, Germany
- acrylonitrile butadiene styrene (ABS), available as Royalite™ (general purpose) from Uniroyal, USA
- 20 - plasticized polyvinylchloride (PVC), available from BGS Kunststoff GmbH, Duesseldorf
- polyamide (PA), available from BGS Kunststoff GmbH
- polyethylene (PE)
- polyethyleneterphthalate (PET)

25

Dynamic shear strength test

An adhesive bond is prepared by adhering a bracket bearing a flat plate having the dimensions 1 mm x 16 mm x 23 mm to 5 mm thick test substrate having the dimensions 30 mm x 80 mm using an adhesive layer 500 µm thick and having the same dimensions as the flat plate of the bracket (16 mm x 23 mm). The test bracket is made of mild steel and is available commercially as A-2516 from R. A. Labone

30

The adhesive layer of the assembly thus prepared was thermally cured using a hand-held device such as that described in copending European patent application no. 96 112 715.6.

- 5 The strength of the adhesive bond was determined by applying cleavage forces to the bond by, first, mechanically engaging one end of a lever arm with the aluminum bracket, and, then, in a 90° fashion while holding the glass substrate stationary, exerting force on the lever arm at a distance of 50 mm from the adhesive bond. Force was applied using an electronic tensile tester having a 5 kN load cell by
10 moving the jaws apart at a rate of 2.5 mm/min until bond failure resulted. The force required to break the bond was recorded in N.

90° peel adhesion test

- 90° Peel adhesive was determined using PSTC-14, a procedure specified in "Test
15 Methods for Pressure Sensitive Adhesive Tapes," 8th edition, available from the Pressure-Sensitive Adhesive Tape Council, 1800 Pickwick Ave., Glenview, IL 600025-1377, U.S.A.

- Layers of the respective adhesives described in the Examples which were protected
20 by two liners, were cut into strips with a width of 12.7 mm. One of the two liners was removed from the adhesive layer and a strip of an aluminum foil (0.135 mm thick, width of 16 mm) was applied to the exposed adhesive by hand pressure. Then the second liner was removed and the exposed adhesive applied to the respective substrate. The assembly thus prepared was passed between the rubber-
25 coated rolls of a laboratory scale laminator (Sallmetal, Raalte, The Netherlands) at a speed of 300 mm/min and a pressure of 2 kg. The assemblies were passed through the laminator twice.

- The construction obtained was allowed to rest in a constant temperature room
30 (23°C, 55% relative humidity) for 30 minutes before testing. The adhesives tested were not thermally cured before the peel adhesion test.

6. EPON 1001, diglycidic ether of bisphenol-A, available from Shell Chemical

Hardeners

- 5 1. A2337XS, Ancamine (TM) modified aliphatic amine, available from Air Products (Manchester, UK)
2. A2014FG, Ancamine (TM) modified aliphatic amine, available from Air Products (Manchester, UK).
3. HT 939, available from Ciba Geigy, Switzerland

10

Photoinitiators

1. 2,2 Dimethoxy-2-phenylacetophenone, available as Irgacure 651 from Ciba Geigy (I 651)
2. 2,2 Dimethoxy-2-phenylacetophenone, available as KB-1 from Sartomer, Exton, PA (KB-1)

15

Crosslinkers

1. 1,6-Hexanediol diacrylate, available from BASF (HDDA)

20 Polymers

1. Polyvinyl acetate, available as Vinnapas UW1 from Wacker Chemie, Burghausen, Germany (UW1)
2. Levapren KA 8479, ethylene vinyl acetate copolymer from Bayer, Leverkusen, Germany; 80% vinyl acetate, 20% ethylene (KA 8479)
- 25 3. Levapren 700 HV, ethylene vinyl acetate copolymer from Bayer, Leverkusen, Germany; 70% vinyl acetate, 30% ethylene (700 HV)
4. Core shell polymer, available as EXL 2691 from Rohm & Haas, Philadelphia, PA, USA (EXL 2691)

Examples 2 - 15 and Comparative Examples 1 - 4

Adhesive layers were prepared according to the method of Example 1, varying the composition as indicated in Table 2. IBA is isobornylacrylate, 2-PhEA is
5 phenoxyethyl acrylate and epoxy (type) and hardener (type), respectively, denote the epoxy resin and the hardener compound, respectively, according to the list "Materials used in the Examples" which was given above.

Onset temperature of the epoxy curing reaction, 90° peel adhesion of the thermally-
10 uncured adhesive and overlap shear strength of the thermally-cured adhesive were measured as described above. The onset temperatures measured in Examples 2-15 were 69-70 °C. The other results are summarized in Table 3.

Comparative Example 5

15 A commercially available high performance acrylic bonding transfer tape (VHB acrylic adhesive tape 4945, available from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota, USA) was subjected to the 90° peel adhesion test and the overlap shear strength test as described under Test Methods above, with the
20 exception that the assembly used for the measurement of overlap was not subjected to thermal curing before overlap shear strength was measured. The results obtained are given in Table 3.

3M Tape 4945 is a non-thermosettable pressure-sensitive adhesive tape and is included as a comparative example to show bond strength and performance of a
25 state-of-the art high performance pressure-sensitive tape which is not thermally curable.

Comparative Example 6

A commercially available thermally-curable epoxy/acrylate pressure-sensitive
30 adhesive transfer tape (3M 9245 SBT available from Minnesota Mining and Manufacturing Co. St. Paul, Minnesota, USA) was subjected to the 90° peel

method "Dynamic Shear Strength Test" and held at an elevated temperature which was varied as described in Table 6. Table 6 also gives the times for which metal bracket was contacted with the heated plate, as well as the respective plastic substrate.

5

The assemblies obtained were subjected to the dynamic shear test described above, and the results are given in Table 6.

10 A layer of the photopolymerized, thermosettable adhesive of Example 21 with a thickness of 500 μm was applied to an aluminum mounting bracket having a round 20 mm diameter base plate) and adhered to a 6 mm thick sheet of float glass. The face of the base plate of the aluminum bracket was then contacted with the hand-held device described in copending European patent application no. 96 112 715.6 to thermally cure the adhesive layer. The contact time and the temperature of the
15 contact means of the hand-held device are varied as specified in Table 7.

The assemblies obtained were subjected to the cleavage strength test described above, and the results are given in Table 7.

20 Examples 22-24

Acrylic monomers as listed in Table 8 were combined with 0.04 pph of Irgacure 651 photoinitiator. The mixture was purged with nitrogen for 30 minutes and then exposed to low intensity ultraviolet radiation as described in Example 1 until a low viscosity syrup was obtained. To this syrup were added in the amounts listed in
25 Table 8: N-vinyl caprolactam (NVC), epoxy resin, 0.1 pph crosslinker HDDA, 0.16 pph additional photoinitiator Irgacure 651, epoxy hardener. The mixture was stirred until homogeneous.

Onset temperature of the epoxy curing reaction, 90° peel adhesion of the thermally-
30 uncured adhesive and dynamic shear strength of the thermally-cured adhesive was measured as described above. The results are summarized in Table 9.

TABLE 1
FEDORS' SOLUBILITY PARAMETERS OF ACRYLATE MONOMERS

| Monomer | Solubility Parameter (cal/cm ³) ^{0.5} |
|---|---|
| Octadecyl acrylate (ODA) | 8.99 |
| Lauryl acrylate (LA) | 9.15 |
| Iso-octyl acrylate (IOA) | 9.22 |
| 2-ethylhexyl acrylate (2-EHA) | 9.22 |
| Tert-Butyl acrylate (TBA) | 9.36 |
| Iso-Butyl acrylate (PHA) | 9.57 |
| Butyl acrylate (BA) | 9.77 |
| Propyl acrylate (PA) | 9.95 |
| Ethyl acrylate (EA) | 10.20 |
| | |
| 3,3,5 trimethylcyclohexyl acrylate (TMCA) | 9.35 |
| Iso-bornyl acrylate (IBA) | 9.71 |
| Cyclohexyl acrylate | 10.16 |
| N-octyl acrylamide (NOA) | 10.33 |
| Tetrahydrofurfuryl acrylate (HFA) | 10.53 |
| Methyl acrylate (MA) | 10.56 |
| 2-Phenoxyethylacrylate (2-PhEA) | 11.03 |
| Phenyl acrylate (PHA) | 11.19 |
| Glycidyl acrylate (GA) | 11.32 |
| N-vinylcaprolactam (NVC) | 12.10 |
| N,N-Dimethylacrylamide (DMA) | 12.32 |
| Butoxy acrylate (BOA) | 12.99 |
| N-vinyl-2-pyrrolidone (NVP) | 13.38 |
| Propoxy acrylate (POA) | 13.62 |
| Acrylic Acid (AA) | 14.04 |
| | |
| Methylmethacrylate (MMA) | 9.93 |
| Ethylmethacrylate (EMA) | 9.72 |
| Propylmethacrylate (PMA) | 9.57 |
| | |
| Vinyl Acetate | 10.56 |
| Styrene | 11.87 |

| Ex | Overlap Shear (N/mm ²) | | | | 90° Peel (N/1.27 cm) | | | | |
|----|------------------------------------|-----|------|-----|----------------------|------|-----|----|----|
| | Al | PC | pMMA | PVC | PC | pMMA | PVC | PE | Al |
| 15 | 7.6 | 4.4 | | | 7 | | | | 13 |
| C1 | 0.02 | | | | | | | | |
| C2 | 0.02 | | | | | | | | |
| C3 | 2.3 | 1.9 | 1.7 | 1.2 | 15 | 14 | 6 | 5 | |
| C4 | 1.3 | 1.3 | 1.1 | 1.0 | 15 | 15 | 6 | 5 | |
| C5 | 1 | 1 | 1 | 1 | 23 | 24 | 8 | 4 | |
| C6 | 11 | 1.3 | 1.6 | **) | 28 | 24 | 7 | 3 | |

***) No measurement possible. PVC melts at the required curing temperature (160°C)

5

TABLE 4

| Ex | IBA [%] | 2-PheEA [%] | Epoxy (type) [%] | Hardener (type) [%] | R972 [%] | Polymer (type) [%] | I 651 *) [pph] | HDHA *) [pph] |
|----|---------|-------------|------------------|---------------------|----------|--------------------|----------------|---------------|
| 16 | 18.5 | 24.6 | 37.1(1) | 17.7(1) | 2.1 | 0 | 0.2 | 0.1 |
| 17 | 17.4 | 23.2 | 34.8(1) | 16.6(1) | 4.0 | 4.0 (1) | 0.2 | 0.1 |
| 18 | 18.1 | 24.1 | 36.3(1) | 17.3(1) | 2.1 | 2.1 (1) | 0.2 | 0.1 |
| 19 | 18.5 | 24.6 | 37.1(1) | 17.6(1) | 0 | 2.2 (1) | 0.2 | 0.1 |
| 20 | 16.3 | 21.8 | 34.2(1) | 16.3(1) | 3.8 | 7.6 (4) | 0.2 | 0.1 |
| 21 | 23.7 | 18.0 | 35.7(1) | 17.0(1) | 4.1 | 1.5 (1) | 0.2 | 0.1 |

*) The masses of the photoinitiator and the crosslinker are disregarded when calculating the mass percentages [%] of the other compounds.

10

TABLE 5

| Ex | Overlap Shear (N/mm ²) | | | | | 90° Peel (N/1.27 cm) | | | | |
|----|------------------------------------|-----|------|------|------|----------------------|------|-----|----|----|
| | Al | PC | pMMA | PVC | ABS | PC | pMMA | PVC | PE | Al |
| 16 | 8.8* | 3.8 | 6.5 | 5.3* | 6.2 | | | | | 14 |
| 17 | 5.9* | 4.4 | 6.9 | 4.3* | 6.3 | | | | | 16 |
| 18 | 8.0 | 4.2 | 6.1 | 4.7* | 6.0 | | | | | 18 |
| 19 | 7.9 | 3.6 | 4.6 | 4.0* | 4.6 | | | | | 13 |
| 20 | 4.7* | 3.4 | 4.1* | 4.3* | 5.8* | 13 | | | | 19 |

* adhesive failure or mixed adhesive/cohesive failure

TABLE 8

| Ex | IBA, % | 2-PhEA, % | NVC, % | Epoxy resin, % (type) | Hardener compound, % (type) |
|----|--------|-----------|--------|-----------------------|-----------------------------|
| 22 | 16 | 23 | 3 | 39 | 19 |
| 23 | 16 | 23 | 2 | 40 | 19 |
| 24 | 16 | 24 | 1 | 40 | 19 |

TABLE 9

| Example | 90° Peel (N / 1.27 cm) | | Dynamic shear (N / mm ²) | | |
|---------|------------------------|------|--------------------------------------|------|------|
| | PMMA | Al | PMMA | PC | Al |
| 22 | 16.2 | 12.9 | 4.47 | 3.81 | 5.31 |
| 23 | 14.6 | 12.3 | 3.09 | 1.89 | 3.96 |
| 24 | 12.4 | 11.0 | 3.24 | 1.63 | 3.90 |

5

TABLE 10

| Ex | BA [%] | NVC [%] | Epoxy resin (type) [%] | Hardener (type) [%] | Polymer (type) [%] | Filler (type) [%] | KB-1 *) [pph] | HDDA *) [pph] |
|----|--------|---------|------------------------|---------------------|--------------------|--------------------|---------------|---------------|
| 25 | 32.2 | 9 | 23.2 (5) 12.9 (6) | 12.4 (3) | 10.3 (1) | | 0.2 | 0.047 |
| 26 | 31.8 | 8.9 | 22.8 (5) 12.7 (6) | 13.7 (1) | 10.1 (2) | | 0.3 | 0.047 |
| 27 | 31.8 | 8.9 | 22.8 (5) 12.7 (6) | 13.7 (1) | 10.1 (3) | | 0.3 | 0.047 |
| 28 | 30.8 | 8.6 | 22.2 (5) 12.3 (6) | 13.3 (1) | 9.8 (1) | 2.5 (1) 0.5 (2) | 0.3 | 0.047 |
| 29 | 33.1 | 8.8 | 19.8 (5) 19.8 (6) | 10.9 (1) | 4.6 (1) | 2.3 (1) 0.7 (2) | 0.3 | 0.047 |
| 30 | 28.9 | 8.5 | 26.4 (5) 8.5 (6) | 12 (1) | 12.5 (1) | 2.5 (1) 0.7 (2) | 0.3 | 0.047 |
| 31 | 35.6 | 10.5 | 17.8 (5) 17.8 (6) | 9.9 (1) | 5.1 (1) | 2.5 (1) 0.8 (2) | 0.3 | 0.047 |
| C7 | 35.6 | 2.7 | 17.9 (5) 17.9 (6) | 9.9 (1) | 12.5 (1) | 2.5 (1) 0.8 (2) | 0.3 | 0.047 |

*) The masses of the photoinitiator and the crosslinker are disregarded when calculating the mass percentages [%] of the components with respect to the mass of the adhesive

10

PATENT CLAIMS

1. Photopolymerizable precursor of a pressure-sensitive thermosettable adhesive
said precursor comprising

5

- (i) from about 30% to about 80% by weight with respect to the mass of the precursor of a photopolymerizable component, comprising a monomeric or prepolymeric syrup, said component exhibiting an overall solubility parameter of between 10 and 11 and comprising (A) at least 30% by weight with respect to the mass of the photopolymerizable component (i) of one or more ethylenically unsaturated monomers with a solubility parameter of between 10 and 11.5 and less than 10% by weight with respect to the mass of component (i) of one or more ethylenically unsaturated compounds with a solubility parameter of more than 11.5, or
- 10 (B) at least 50% by weight with respect to the mass of the photopolymerizable compound (i) of one or more ethylenically unsaturated monomers with a solubility parameter of between 9.5 and 11.5 and 10-30% by weight with respect to the mass of the photopolymerizable component (i) of one or more ethylenically unsaturated compounds with a solubility parameter of between 11.5 and 12.5 provided that in case (B) the precursor comprises between 3-15% by weight with respect to the mass of the precursor of one or more polymers with a solubility parameter of 10-12.5,
- 15
- 20
- 25 (ii) from about 20 to about 70% by weight with respect to the mass of the precursor of one or more epoxy resins and/or monomers,
- (iii) an effective amount of one or more photoinitiators, and
- 30 (iv) an effective amount of one or more nucleophilic latent hardeners for the epoxy resins and/or epoxy-containing monomers which hardeners are

6. Thermosettable pressure-sensitive adhesive according to claim 5 which exhibits a percentage of remaining reaction of at least 90% after 8 weeks of storage.
7. Thermoset adhesive which is obtainable by thermally curing the thermosettable pressure-sensitive adhesive according to claims 5 or 6.
8. A method for bonding a plastic surface to another surface comprising
 - (i) sandwiching a layer of a pressure-sensitive thermosettable adhesive according to any of claims 5 or 6 between the two surfaces, and
 - (ii) heating the assembly to a temperature above the onset temperature of the epoxy curing reaction.
9. Assembly comprising two plastic surfaces which are bonded with a thermoset adhesive the precursor of which comprises a blend of an acrylic-based pressure-sensitive adhesive and one or more thermosettable epoxy resins and/or monomers and is cured at a temperature above the onset temperature of the epoxy curing reaction of below 100°C to give an overlap shear strength of the assembly of at least 3 MPa.
10. Assembly comprising at least one plastic surface which is obtained by
 - (i) sandwiching a layer of a pressure-sensitive thermosettable adhesive according to any of claims 5 or 6 between the two surfaces, and
 - (ii) heating the assembly at a temperature above the onset temperature of the epoxy curing reaction.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/18841

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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